

Entanglement as Measure of Electron-Electron Correlation in Quantum Chemistry Calculations

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Abstract

In quantum chemistry calculations, the correlation energy is defined as the difference between the Hartree-Fock limit energy and the exact solution of the nonrelativistic Schrödinger equation. With this definition, the electron correlation effects are not directly observable. In this report, we show that the entanglement can be used as an alternative measure of the electron correlation in quantum chemistry calculations. Entanglement is directly observable and it is one of the most striking properties of quantum mechanics. As an example we calculate the entanglement for He atom and H₂ molecule with different basis sets.

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The Hartree-Fock self-consistent field approximation, which is based on the idea that we can approximately describe an interacting fermion system in terms of an effective single-particle model, remains the starting point and the major approach for quantitative electronic structure calculations. In quantum chemistry calculations, the correlation energy is defined as the energy error of the Hartree-Fock wave function, i.e., the difference between the Hartree-Fock limit energy and the exact solution of the nonrelativistic Schrödinger equation¹. There also exists other measures of electron correlation in the literature such as the statistical correlation coefficients² and more recently the Shannon entropy as a measure of the correlation strength^{3,4}. Electron correlations have a strong influence on many atomic, molecular⁵, and solid properties⁶. Recovering the correlation energy for large systems remains one of the most challenging problems in quantum chemistry.

The concept of electron correlation as defined in quantum chemistry calculations is useful but not directly observable, i.e., there is no operator in quantum mechanics that its measurement gives the correlation energy. In this letter, we propose to use the entanglement as a measure of the electron correlation. Entanglement is directly observable and it is one of the most striking properties of quantum mechanics.

It was nearly 70 years ago when Schrödinger gave the name "entanglement" to a correlation of quantum nature. He stated that for an entangled state "the best possible knowledge of the whole does not include the best possible knowledge of its parts"⁷. Over the decades the meaning of the word "entanglement" has changed its flavor and our view of the nature of entanglement may continue to be modified⁸. Entanglement is a quantum mechanical property that describes a correlation between quantum mechanical systems that has no classical analog^{9,10,11,12}. A pure state of a pair of quantum systems is called entangled if it is unfactorizable, as for example, the singlet state of two spin- $\frac{1}{2}$ particles, $\frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)$. A mixed state is entangled if it can not be represented as a mixture of factorizable pure states^{13,14,15}. Since the seminal work of Einstein, Podolsky, and Rosen¹⁶ there has been a quest for generating entanglement between quantum particles^{10,17}. Investigation of quantum entanglement is currently a very active area and has been studied intensely due to its potential applications in quantum communications and information processing¹⁰ such as quantum teleportation^{18,19}, superdense coding²⁰, quantum key distribution²¹, telecloning, and decoherence in quantum computers^{22,23,24}.

In order to employ the entanglement as an alternative method of measuring the electron

correlation, we present the scheme to quantify entanglement based on the entanglement measure for two-particle systems^{25,26}. We will obtain a general approach to quantify the entanglement between different spin-orbitals of atomic and molecular systems.

For two electron system in $2m$ -dimensional spin-space orbital with c_a and c_a^\dagger denote the fermionic annihilation and creation operators of single-particle states and $|0\rangle$ represents the vacuum state, a pure two-electron state $|\Phi\rangle$ can be written as

$$|\Phi\rangle = \sum_{a,b \in \{1,2,3,4,\dots,2m\}} \omega_{a,b} c_a^\dagger c_b^\dagger |0\rangle \quad (1)$$

where a, b run over the orthonormalized single particle states, and Pauli exclusion requires that the $2m \times 2m$ expansion coefficient matrix ω is antisymmetric: $\omega_{a,b} = -\omega_{b,a}$, and $\omega_{i,i} = 0$.

In the occupation number representation $(n_1 \uparrow, n_1 \downarrow, n_2 \uparrow, n_2 \downarrow, \dots, n_m \uparrow, n_m \downarrow)$, where \uparrow and \downarrow mean α and β electrons respectively, the subscripts denote the spatial orbital index and m is the total spatial orbital number. By tracing out all other spatial orbitals except n_1 , we can get a (4×4) reduced density matrix for the spatial orbital n_1

$$\rho_{n_1} = Tr_{n_1} |\Phi\rangle \langle \Phi| = \begin{pmatrix} \rho_{n_1,0} & 0 & 0 & 0 \\ 0 & 4 \sum_{i=1}^{m-1} |\omega_{2,2i+1}|^2 & 0 & 0 \\ 0 & 0 & 4 \sum_{i=2}^m |\omega_{1,2i}|^2 & 0 \\ 0 & 0 & 0 & \rho_{n_1,2} \end{pmatrix}, \quad (2)$$

where $\rho_{n_1,0}$ denotes an "empty orbital",

$$\rho_{n_1,0} = 4 \sum_{i=1}^{m-1} \sum_{j=1}^{m-1} |\omega_{2i+1,2j+2}|^2 \quad (3)$$

and $\rho_{n_1,2}$ denotes "two electron occupied orbital",

$$\rho_{n_1,2} = 4|\omega_{1,2}|^2. \quad (4)$$

The "one electron occupied orbital", in (\uparrow, \downarrow) basis set is given by

$$\rho_{n_1,1} = \begin{pmatrix} 4 \sum_{i=1}^{m-1} |\omega_{2,2i+1}|^2 & 0 \\ 0 & 4 \sum_{i=2}^m |\omega_{1,2i}|^2 \end{pmatrix}, \quad (5)$$

The matrix elements of ω can be calculated from the expansion coefficient of the ab initio Configure Interaction (CI) method. The CI wave function with single and double excitation can be written as

$$|\Phi\rangle = c_0|\Psi_0\rangle + \sum_{ar} c_a^r |\Psi_a^r\rangle + \sum_{a<b, r<s} c_{a,b}^{r,s} |\Psi_{a,b}^{r,s}\rangle, \quad (6)$$

where $|\Psi_0\rangle$ is the ground state Hartree-Fock wave function, c_a^r is the coefficient for single excitation from orbital a to r , and $c_{a,b}^{r,s}$ is the double excitation from orbital a and b to r and s . Now the matrix elements of ω can be written in terms of the CI expansion coefficients

$$\omega_{1,2} = \frac{c_0}{2}, \quad \omega_{2,2i+1} = \frac{c_1^{2i+1}}{2}, \quad \omega_{1,2i+2} = \frac{c_2^{2i+2}}{2}, \quad \omega_{2i+1,2j+2} = -\frac{c_{1,2}^{2i+1,2j+2}}{2}, \quad (7)$$

where $i, j = 1, 2, \dots, m$. In this general approach, the ground state entanglement is given by von Neumann entropy of the reduced density matrix ρ_{n1}

$$S(\rho_{n1}) = -\text{Tr}(\rho_{n1} \log_2 \rho_{n1}). \quad (8)$$

We are now ready to evaluate the entanglement for the H_2 molecule as a function of R using a direct and simpler approach based on the two-electron density matrix calculated from the CI wave function with single and double electronic excitations. In the occupation number representation, the CI wave function is given by

$$|\Phi\rangle = c_0|1100\dots\rangle + c_1^3|0110\dots\rangle + c_2^4|1001\dots\rangle + c_{1,2}^{3,4}|0011\dots\rangle + \dots \quad (9)$$

By tracing out all other orbitals except 1, we can get the reduced density matrix for $(n_1 \uparrow = 0, 1)$

$$\rho_1 = \text{Tr}_1 |\Phi\rangle\langle\Phi| = \begin{pmatrix} \sum_{i=1}^{m-1} |c_1^{2i+1}|^2 + \sum_{i=1}^{m-1} |c_{1,2}^{2i+1,2i+2}|^2 & 0 \\ 0 & |c_0|^2 + \sum_{i=1}^{m-1} |c_2^{2i+2}|^2 \end{pmatrix}. \quad (10)$$

The CI wave function expansion coefficients are calculated with the electronic structure package Gaussian²⁷. Thus the entanglement of H_2 molecule is readily calculated by the von Neumann entropy

$$S(\rho_1) = -\text{Tr}(\rho_1 \log_2 \rho_1). \quad (11)$$

Figure (1) shows the calculated entanglement S for H_2 molecule, Eq. (11), as a function of the internuclear distance R using Gaussian basis set 3-21G²⁷. For comparison we included the usual electron correlation ($E_c = |E^{\text{Exact}} - E^{\text{UHF}}|$) and spin-unrestricted Hartree-Fock (UHF) calculations²⁷ using the same basis set in the figure. At the limit $R = 0$, the dot represents the electron correlation for the He atom, $E_c = 0.0149(a.u.)$ using 3-21G basis

set compared with the entanglement for the He atom $S = 0.0313$. With a larger basis set, $cc - pV5Z^{28}$, we obtain numerically $E_c = 0.0415(a.u.)$ and $S = 0.0675$. Thus, qualitatively entanglement and absolute correlation have similar behavior. At the united atom limit, $R \rightarrow 0$, both have small values, then rise to a maximum value and finally vanishes at the separated atom limit, $R \rightarrow \infty$. However, note that for $R > 3\text{\AA}$ the correlation between the two electrons is almost zero but the entanglement is maximal until around $R \sim 4\text{\AA}$, the entanglement vanishes for $R > 4\text{\AA}$.

To understand the entanglement behavior for H_2 molecule using ab initio quantum chemistry methods, we calculate the entanglement for a simpler two-electron model system. This is a model of two spin- $\frac{1}{2}$ electrons with an exchange coupling constant J (a.u.) in an effective transverse magnetic field of strength B (a.u.). In order to describe the environment of the electrons in a molecule, we simply introduce a small effective external magnetic field B . The general Hamiltonian for such a system is given by

$$H = -\frac{J}{2}(1 + \gamma)\sigma_1^x \otimes \sigma_2^x - \frac{J}{2}(1 - \gamma)\sigma_1^y \otimes \sigma_2^y - B\sigma_1^z \otimes I_2 - BI_1 \otimes \sigma_2^z, \quad (12)$$

where σ^a are the Pauli matrices(a= x,y,z) and γ is the degree of anisotropy. For $\gamma = 1$ Eq.(12) reduces to the Ising model, whereas for $\gamma = 0$ it is the XY model.

Our two spin problem admits an exact solution, it is simply a (4×4) matrix with the following four eigenvalues

$$\lambda_1 = -J, \lambda_2 = J, \lambda_3 = -\sqrt{4B^2 + J^2\gamma^2}, \lambda_4 = \sqrt{4B^2 + J^2\gamma^2} \quad (13)$$

and the corresponding eigenvectors

$$|\phi_1\rangle = \begin{pmatrix} 0 \\ 1/\sqrt{2} \\ 1/\sqrt{2} \\ 0 \end{pmatrix}, |\phi_2\rangle = \begin{pmatrix} 0 \\ -1/\sqrt{2} \\ 1/\sqrt{2} \\ 0 \end{pmatrix}, |\phi_3\rangle = \begin{pmatrix} \sqrt{\frac{\alpha+2B}{2\alpha}} \\ 0 \\ 0 \\ \sqrt{\frac{\alpha-2B}{2\alpha}} \end{pmatrix}, |\phi_4\rangle = \begin{pmatrix} -\sqrt{\frac{\alpha-2B}{2\alpha}} \\ 0 \\ 0 \\ \sqrt{\frac{\alpha+2B}{2\alpha}} \end{pmatrix}, \quad (14)$$

where $\alpha = \sqrt{4B^2 + J^2\gamma^2}$. In the basis set $\{|\uparrow\uparrow\rangle, |\uparrow\downarrow\rangle, |\downarrow\uparrow\rangle, |\downarrow\downarrow\rangle\}$, the eigenvectors can be written as

$$|\phi_1\rangle = \frac{1}{\sqrt{2}}(|\downarrow\uparrow\rangle + |\uparrow\downarrow\rangle), \quad (15)$$

$$|\phi_2\rangle = \frac{1}{\sqrt{2}}(|\downarrow\uparrow\rangle - |\uparrow\downarrow\rangle), \quad (16)$$

$$|\phi_3\rangle = \sqrt{\frac{\alpha - 2B}{2\alpha}}|\downarrow\downarrow\rangle + \sqrt{\frac{\alpha + 2B}{2\alpha}}|\uparrow\uparrow\rangle, \quad (17)$$

$$|\phi_4\rangle = \sqrt{\frac{\alpha + 2B}{2\alpha}}|\downarrow\downarrow\rangle - \sqrt{\frac{\alpha - 2B}{2\alpha}}|\uparrow\uparrow\rangle. \quad (18)$$

Now we confine our interest to the calculation of the entanglement between the two electronic spins. For simplicity we take $\gamma = 1$, Eq. (12) reduces to the Ising model with the ground state energy λ_3 and the corresponding eigenvector $|\phi_3\rangle$. All the information needed for quantifying the entanglement in this case is contained in the two-electron density matrix.

When a biparticle quantum system AB is in a pure state there is essentially a unique measure of the entanglement between the subsystems A and B given by the von Neumann entropy S^{29} . If we denote ρ_A the partial trace of ρ_{AB} with respect to subsystem B, $\rho_A = \text{Tr}_B(\rho_{AB})$, the entanglement of the state ρ_{AB} is defined as the von Neumann entropy of the reduced density operator ρ_A , $S(\rho_{AB}) \equiv -\text{Tr}[\rho_A \log_2 \rho_A]$.

For our model system in the ground state $|\phi_3\rangle$, the reduced density matrix in the basis set (\uparrow, \downarrow) is given by

$$\rho_A = \begin{pmatrix} \frac{\alpha+2h}{2\alpha} & 0 \\ 0 & \frac{\alpha-2h}{2\alpha} \end{pmatrix}. \quad (19)$$

Thus, the entanglement is simply given by

$$S = -\frac{1}{2}\log_2\left(\frac{1}{4} - \frac{1}{4+\lambda^2}\right) + \frac{1}{\sqrt{4+\lambda^2}}\log_2\frac{\sqrt{4+\lambda^2}-2}{\sqrt{4+\lambda^2}+2} \quad (20)$$

where $\lambda = J/B$.

The value of J , the exchange coupling constant between the spins of the two electrons, can be calculated as half the energy difference between the lowest singlet and triplet states of the hydrogen molecule. Herring and Flicker have shown³⁰ that J for H_2 molecule can be approximated as a function of the interatomic distance R . In atomic units, the expression for large R is given by

$$J(R) = -0.821 R^{5/2} e^{-2R} + O(R^2 e^{-2R}). \quad (21)$$

Figure (2) shows the calculated von Neumann Entanglement (S), Eq. (20), as a function of the distance between the two electronic spins R , using $J(R)$ of Eq. (21), for different

values of the magnetic field strength B . At the limit $R \rightarrow \infty$ the exchange interaction J vanishes as a result the two electronic spins are up and the wave function is factorizable, i.e. the entanglement is zero. At the other limit, when $R = 0$ the entanglement is zero for this model because $J = 0$. As R increases, the exchange interaction increases leading to increasing entanglement between the two electronic spins. However this increase in the entanglement reaches a maximum limit as shown in the figure. For large distance, the exchange interaction decreases exponentially with R and thus the decrease of the entanglement. The figure also shows that the entanglement increases with decreasing the magnetic field strength. This can be attributed to effectively increasing the exchange interaction. Thus we get the similar behavior as the entanglement for the H_2 molecule as a function of the internuclear distance R , using accurate ab initio methods. Because the Eq. (21) is only applicable to the large value of R , it is not surprising to see, in the limit $R \rightarrow 0$, the entanglement converges to the He atom results in ab initio methods but disappears in this simple model.

Recently a new promising approach is emerging for the realization of quantum chemistry calculations without wave functions through first order semidefinite programming³¹. The electronic energies and properties of atoms and molecules are computable simply from an effective two-electron reduced density matrix $\rho_{(AB)}$. Thus, the electron correlation can be directly calculated as effectively with the entanglement between the two electrons, which is readily calculated as the von Neumann entropy $S = -Tr \rho_A \log_2 \rho_A$, where $\rho_A = Tr_B \rho_{(AB)}$. Utilizing this combined approach, one calculates the electronic energies and properties of atoms and molecules including correlation without wave functions or Hartree-Fock reference systems.

In summary, we presented the entanglement as an alternative measure of the electron electron correlation in quantum chemistry calculations for atoms and molecules. All the information needed for quantifying the entanglement is contained in the two-electron density matrix. This measure is readily calculated by evaluating the von Neumann entropy of the one electron reduced density operator. This definition of correlation has deep roots in quantum theory, observable, and does need a reference system such as Hartree-Fock calculations. The approach is general and can be used for larger atomic and molecular systems.

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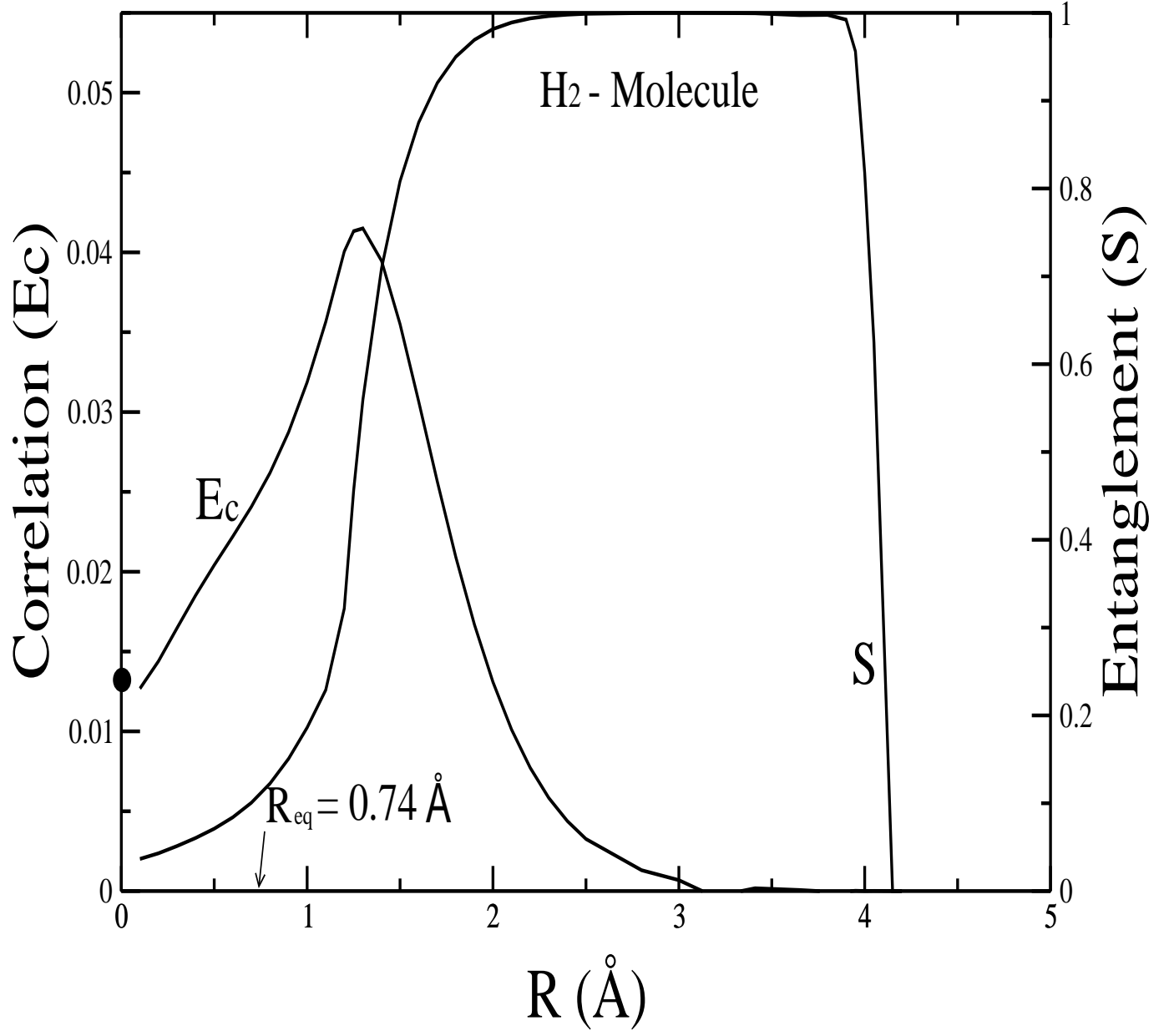


FIG. 1: Comparison between the absolute value of the electron correlation $E_c = |E^{Exact} - E^{UHF}|$ and the von Neumann Entanglement (S) as a function of the internuclear distance R for the H_2 molecule using Gaussian basis set 3-21G. At the limit $R = 0$, the dot represents the electron correlation for the He atom, $E_c = 0.0149(a.u.)$ using 3-21G basis set compared with the entanglement for He atom $S = 0.0313$. The equilibrium distance using 3-21G basis set is $R_{eq} = 0.74\text{\AA}$

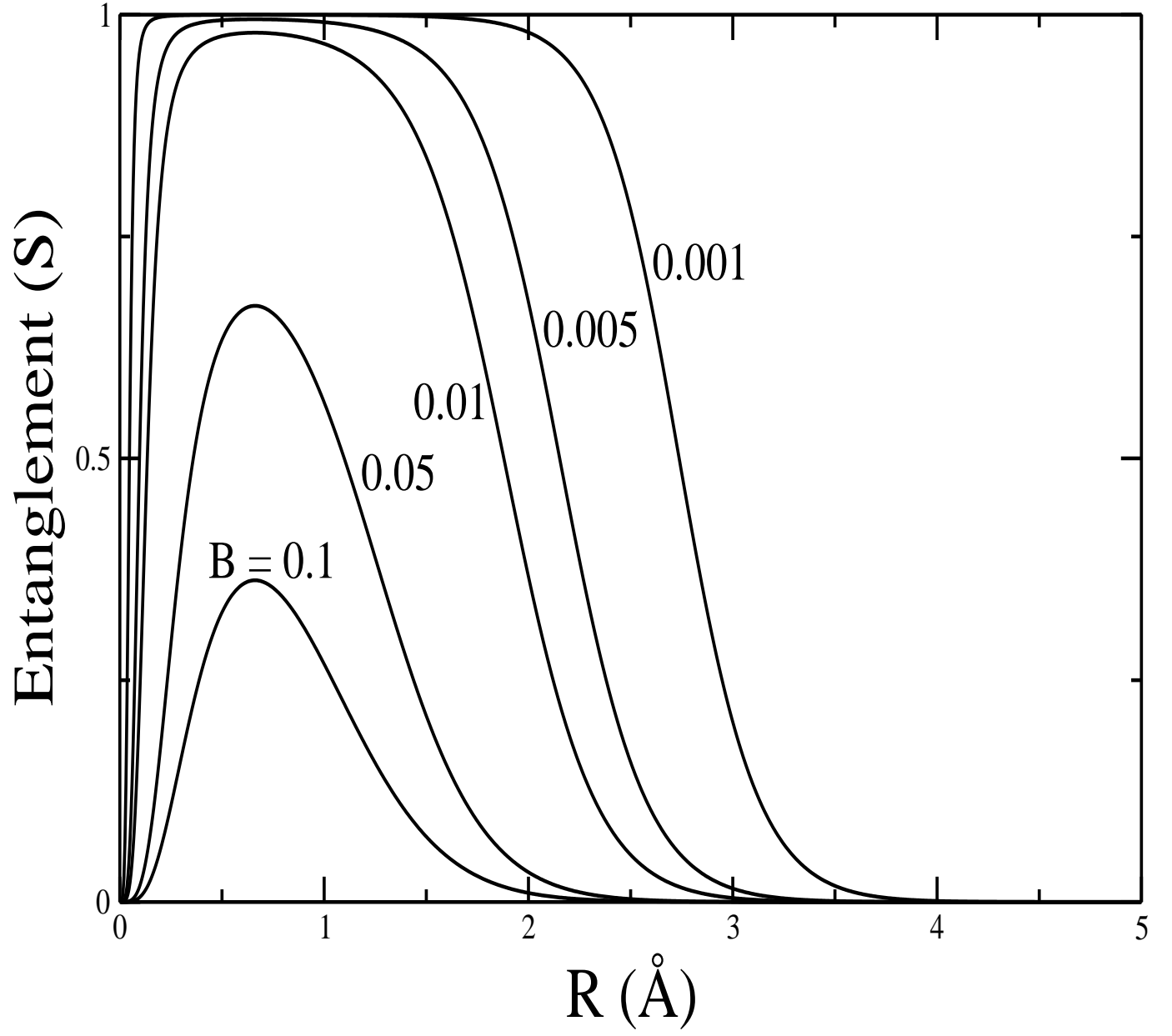


FIG. 2: von Neumann Entanglement (S) as a function of the distance R between the two spins for different values of the magnetic field strength B .